

SIMULATION AND ENVIRONMENTAL ASSESSMENT OF BIODIESEL USING SUPERCRITICAL METHANOL

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KA09124

A proposal submitted in fulfillment of the
Requirements for completing the assessment of

Final Year Project (PSM 2)

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FEBRUARY 2013

ABSTRACT

Biodiesel is a recommended petroleum-based diesel substitute mainly because it is environmentally friendly and is renewable, domestic resource. In this thesis, supercritical methanol process to produce biodiesel from the rapeseed was design and simulate by using Aspen Plus v 7.0. Process flowsheets, along with detailed operating conditions and equipment design for this process was created. An environment assessment was also performed based on the result of process simulations and compare with heterogeneous catalyst method. WAR algorithm method is applied to perform environment assessment. The simulation results showed the supercritical process with 42:1 molar ratio and working at 350⁰C and 430 bar produce 997.91kg/h of FAME. . The environmental impact assessment shows the heterogeneous catalyst process show the least PEI result compare to supercritical methanol process which is indicate TRO 1552.33(with product) and TRO 1668.01(with product) respectively.

ABSTRAK

Biodiesel merupakan pengganti diesel berasaskan petroleum yang disyorkan terutamanya kerana ia adalah mesra alam dan boleh diperbaharui serta sumber domestik. Dalam tesis ini, Aspen Plus v 7.0 digunakan untuk process simulasi berasaskan biji sawi untuk menghasilkan biodiesel melalui process superkritikal methanol. Diagram proses, serta keadaan operasi yang terperinci dan reka bentuk peralatan untuk proses ini telah dicipta. Melalui penilaian teknikal proses ini menunjukkan bahawa dengan menggunakan metanol superkritikal, ia menghasilkan product yang tinggi dan jangka masa process adalah singkat. Satu penilaian persekitaran juga telah dilakukan berdasarkan hasil simulasi proses dan perbandingan kaedah heterogeneous catalyst dibuat untuk tujuan pembelajaran. Kaedah WAR algoritma digunakan untuk penilaian alam sekitar. Keputusan simulasi menunjukkan proses ini dengan nisbah molar 42:1 dan beroperasi pada 350⁰C dan 430 bar berjaya menghasilkan 997.91kg/Jam biodiesel. Berdasarkan keputusan kajian alam sekitar, keputusan menunjukkan bahawa kaedah heterogeneous adalah paling kurang kesan terhadap alam sekitar berbanding dengan kaedah superkritikal methanol dengan menunjukkan bacaan masing-masing pada TRO 1552.33(produk) dan TRO 1668.01(produk).

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LIST OF ABBREVIATION

WAR	-	Waste Reduction
ASTM	-	American Society for Testing and Materials
FAME	-	Fatty Acid Methyl Esters
FFA	-	Free Fatty Acids
SCM	-	Supercritical Methanol Method
PEI	-	Potential Environment Impact
GWP	-	Global Warming Potential
ODP	-	Ozone Depletion Potential
AP	-	Acidification Or Acid Rain Potential
PCOP	-	Photochemical Oxidation
HTPI	-	Human Toxicity By Ingestion
HTPE	-	Human Toxicity By Inhalation Or Dermal Exposure
ATP	-	Aquatic Toxicity Potential
TTP	-	Terrestrial Toxicity Potential
TRO	-	Total Rate Output

CHAPTER 1

INTRODUCTION

1.1 Background of study

Biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl esters. Typically, it made by chemically reacting lipids such as vegetable oil, animal fat with an alcohol to produce fatty acid esters (Zhang *et al.*, 2002). Biodiesel used in standard diesel engines and it is derived from the vegetable and waste oils used to fuel converted diesel engines. Biodiesel can be used alone, or blended with petro diesel. Because its primary feedstock is a vegetable oil or animal fat, biodiesel is generally considered to be renewable. Since the carbon in the oil or fat originated mostly from carbon dioxide in the air, biodiesel is considered to contribute much less to global warming than fossil fuels. Homogeneous acid and alkali process design are conventional methods that are widely used in industry. However, heterogeneous catalysis and supercritical methanol process have been reviewed to show advantageous over the conventional process.

In this paper, based on study done by Othman *et al.* (2011) a biodiesel production plant was developed using supercritical methanol and acid oils as raw materials. A process simulator was employed to produce the conceptual design and simulate using Aspen Plus software. By using these models also, it was possible to perform environmental assessment. The supercritical alternative appears as a good technical possibility to produce biodiesel.

1.2 Problem statement

Environmental assessment was rarely introduced in a process design. Environmental concern received more attention in recent years thus implementing environmental assessment is an advantage in process design.

In environmental assessment of process design, common environmental performance used was LCA which was time consuming and costly. Alternatively, WAR algorithm was used as it is best performed during designing stage due to the simpler approaches (Othman *et al.*, 2011). Environmental assessment using WAR algorithm method determined the potential environmental impact (PEI) through a process thus help to evaluate the effect that the mass of the process would have on the environment if they were to be emitted to the environment.

1.3 Research objectives

1. Simulation and modeling of biodiesel via supercritical system using Aspen Plus software
2. To evaluated environmental assessment using waste reduction analysis (WAR) algorithms

1.4 Scopes of the proposal study

In this study, continuous process of biodiesel production at a rate of 8000 tonnes/year using supercritical methanol is modeled and simulated based on the design and parameters referred from Lim *et al.* (2009) and Othman *et al.* (2011). Results from simulation are then used to perform economic and environmental analysis. The scopes of this study include:

- i. Develop and modeling the continuous process flowsheets of supercritical biodiesel process using Aspen Plus V7.0
- ii. Determine the potential environment impact (PEI) of biodiesel process using WAR algorithm method performed in spreadsheet of Microsoft Excel.

1.5 Significance of the Proposed Study

The significance of this study is to provide another perspective of analyzing process design which is by taking account the environmental criteria. Analyzing of potential environmental impact (PEI) in process design improved the economic and environmental aspect of the process itself.

1.6 Thesis Structure

This thesis consist five chapters which is the introduction, literature review, methodology, result and discussion, and conclusion and recommendation.

Chapter one is divided into six sub chapters which are background of proposed study, problem statement, research objective, scope of the proposed study, significance of the proposed study and thesis structure.

The second chapter consists of introduction, process description, and technology option for biodiesel production, supercritical methanol, and Environment Assessment.

The third chapter is methodology that consist seven part which are introduction, process synthesis, process simulation, chemical component, thermodynamics method and model, process flowsheet diagram, and Environmental assessment.

The fourth chapter is result and discussion. The chapter contains five chapters which are introduction, simulation results, discussion, Environmental assessment and simulation difficulties

For the chapter five is about result and recommendations.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Biodiesel is a renewable and environmentally friendly energy. It is also an important replace for petroleum diesel. According ASTM biodiesel can be defined as monoalkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fatty. It is typically produced by a catalyzed transesterification reaction in which vegetable oil or animal fatty reacts with an alcohol. As an alternative, biodiesel can be in the neat form or mixed with petroleum-based diesel.

Relative conventional petroleum-based fuels, biodiesel has gained acceptance as an alternative fuel because:

- It is renewable, domestic resources. Every country has ability to produce biodiesel because it derived from the vegetable oil and animal fat. Thus it will reduce import of petroleum-based diesel.
- It is biodegradable and non-toxic. According to the European test of biodiesel produced from the rapeseed oil shows that it is 99.6% biodegradable within 21 days and should completely within one month (Congressional Research Service, 1993).
- It produces less carbon monoxide, lower particular matter (e.g smoke), unburned hydrocarbons (e.g soot) and almost no sulfur or aromatic compounds compared to the petroleum diesel. For an engine running on the biodiesel, found a 20% reduction in carbon monoxide emissions (Korbitz *et al.* 1999), 99% reduction in sulfur compounds, and 45% reduction in particulate matter and soot emissions.

- It has a high flash point (approximately 150°C). Petroleum-based diesel has a much lower flash point (approximately 50°C) (Krawczyk *et al.* 1996). Fuels with higher flash points are less volatile and thus, it will safer to transport or handle.

Apart from these good features, biodiesel has some limitations:

- It has poorer low-temperature properties (e.g, higher cloud point) than petroleum-based diesel fuels, which might be a barrier to its use in cold climates. One effective way to overcome this shortcoming is to produce a blend of biodiesel with petroleum-based diesel fuels, such as B20 (20% biodiesel, 80% diesel) (Krawczyk *et al.*, 1996).
- It has slightly higher (3%) emissions of nitrogen oxide (NO₂) than petroleum-based diesel (Krawczyk *et al.*, 1996; Korbitz *et al.*, 1999). However, such small increases could be overcome by adjusting combustion temperature or engine timing (Krawczyk *et al.*, 1996).

In briefly, biodiesel appears to be good alternative to petroleum-based fuel and is being used in many countries, especially in environmentally sensitive areas. The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters and glycerol. Meanwhile, Triglyceride as the main component of vegetable oil, consists of the three long chain fatty acids esterifies to a glycerol backbone. When the triglyceride reacts with an alcohol (methanol), the three fatty acid chains are released from the glycerol skeleton and combine with methanol to yield fatty acid methyl esters (FAME). Glycerol is produced as a by-product. Methanol is most commonly used alcohol due low cost and in this process methanol chooses as the raw material.

2.2 Process Description

Nowadays, most of the biodiesel plant commercially operates based on the alkali-catalyzed. The process involves transesterification reaction in reactor, ester/glycerol separation process, biodiesel refining and glycerol refining. In addition, the raw material for the production of biodiesel are easy to obtain and renewable for example crude vegetable oil, waste cooking oil or animal fat or microalga can use as the raw material or feedstock. Figure 2.1 below shows the basic schematic for biodiesel production.

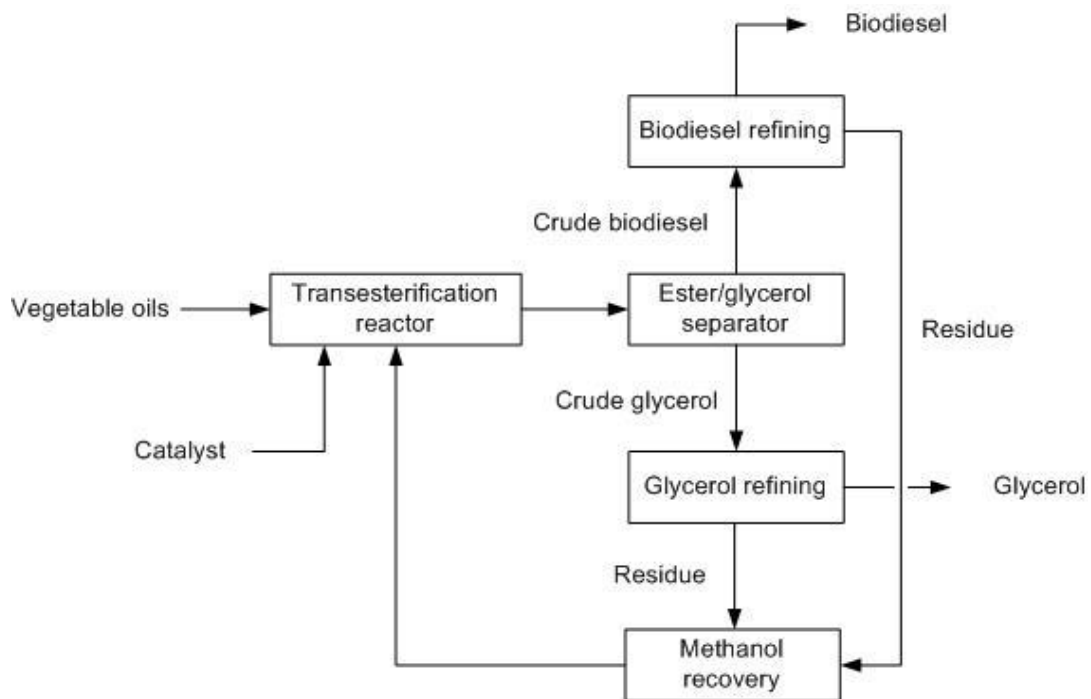


Figure 2.1: Basic schematic for Biodiesel production (Othman *et al.*, 2011)

2.2.1 Transesterification reaction

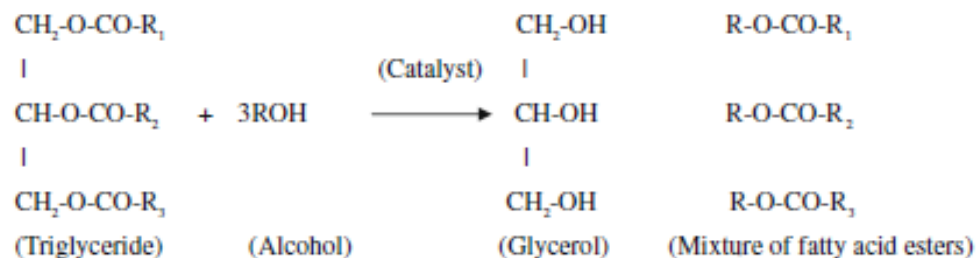


Figure 2.2: Biodiesel reaction. (Leung *et al.*, 2010)

Figure 2.2 above shows the reaction for production of biodiesel through the transesterification reaction. In this reaction the long hydrocarbon chain sometimes called fatty acid chain which is R1, R2, and R3 react with alcohol (methanol) in presence of catalyst such as sodium hydroxide or potassium hydroxide to produce the mixture of ester and Glycerin or Glycerol. The ratio of methanol and oil is 3:1.

According to Leung *et al.* (2010), methanol is the preferred alcohol for producing biodiesel because of its low cost. Normally, there are five main types of chains in vegetable oils and animal oils: palmitic, stearic, oleic, linoleic, and linolenic. The common fatty acid and vegetable oil physicochemical properties are given in table 2.1

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric	0,1	0,1	0,1	0,1	0,1	46,5
Myristic	0,1	0,7	1,0	1,4	2,8	19,2
Palmitic	10,2	20,1	42,8	23,6	23,3	9,8
Stearic	3,7	2,6	4,5	14,2	19,4	3,0
Oleic	22,8	19,2	40,5	44,2	42,4	6,9
Linoleic	53,7	55,2	10,1	10,7	2,9	2,2
Linolenic	8,6	0,8	0,2	0,4	0,9	0,0

Table 2.1: Oil composition for various feedstocks. (F. Ma & M. A. Hanna., 1999)

Vegetable oils and fats may contain small amounts of water and free fatty acids (FFA). For an alkali-catalyzed transesterification, the alkali catalyst that is used will react with the FFA to form soap. The figure 2.3 shows the saponification reaction of the catalyst (sodium hydroxide) and the FFA, forming soap and water.

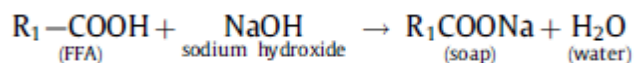


Figure 2.3: Saponification reaction. (Leung et al., 2010)

This reaction is undesirable because the soap lowers the yield of the biodiesel and inhibits the separation of the esters from the glycerol. In addition, it binds with the catalyst meaning that more catalyst will be needed and hence the process will involve a higher cost (Gerpen *et al.*, 2004). Water, originated either from the oils and fats or formed during the saponification reaction, retards the transesterification reaction through the hydrolysis reaction. It can hydrolyze the triglycerides to diglycerides and forms more FFA. The typical hydrolysis reaction is shown in figure 2.4.

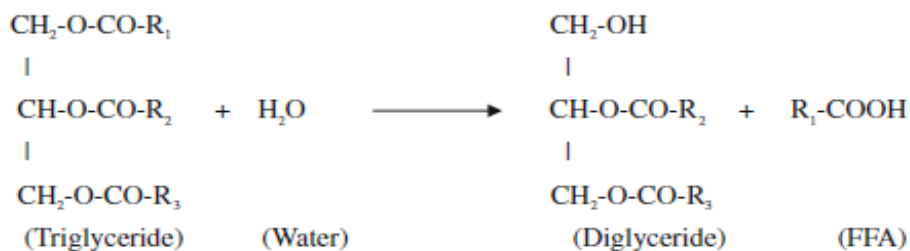


Figure 2.4: Hydrolysis reaction. [Leung *et al.*, 2010]

However, the FFA can react with alcohol to form ester (biodiesel) by an acid-catalyzed esterification reaction. This reaction is very useful for handling oils or fats with high FFA, as figure 2.5 shown in the equation below:

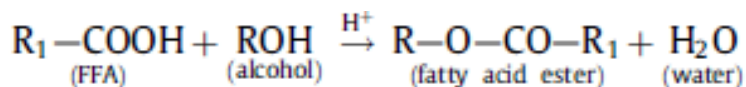


Figure 2.5: Acid-catalyzed esterification reaction. (Leung et al., 2010)

Normally, the catalyst for this reaction is concentrated sulphuric acid. Due to the slow reaction rate and the high methanol to oil molar ratio that is required, acid-catalyzed esterification has not gained as much attention as the alkali-catalyzed transesterification (Soriano *et al.*, 1999).

2.2.2 Ester/glycerol separation

The first step usually employed to recover biodiesel after transesterification reaction is separation of crude biodiesel from by-product, glycerol. The fast separation of biodiesel and glycerol is as a result of differences in their polarities and also significant difference in their densities. The density of biodiesel and glycerol are 0.88 gm/cc and 1.05 gm/cc or more respectively. The density of glycerol is dependent on the amount of water, catalyst and methanol present in it. This density difference is sufficient to employ simple gravity separation technique to separate biodiesel phase from glycerol phase (Gerpen *et al.*, 2004).

2.2.3 Biodiesel refining

The next step after separation process is biodiesel refining process. The process involves the water washing before go through the further refining process in order to produce quality of desired product. The objective for ester washing is to removal any soap that formed during transesterification reaction and also water reacts as the medium to neutralize the remaining catalyst. In addition, the residual methanol should be removed before washing steps in order to

prevent the addition of methanol to the wastewater effluent. There are some types of water that have difference function for the washing steps. In other hand, different types of water that used for washing have difference function for example the uses of warm water (49 to 60°C) to prevents precipitation of saturated fatty acid esters and retards the formation of emulsions with the use of a gentle washing action meanwhile the uses of softened water (slightly acidic) eliminates calcium and magnesium contamination and neutralizes remaining base catalysts.

2.2.4 Side stream management

For biodiesel production there are basically three side streams that must be treated to optimize the stability of a biodiesel plant which are excess methanol, glycerol byproduct and wastewater. These side streams must be treated properly to minimize the environmental impact to the surroundings, especially methanol, which is highly flammable and toxic, and also maximize the profit from recovering glycerol which has higher value than biodiesel. Wastewater constitutes an operating cost for the plant, both of the water consumption of the water treatment cost of the plant.

Since glycerol is treat as by-product which recovered from the tranesterification reaction that contains some impurities of chemical such as residual alcohol, catalyst residue, oil and some ester. The by-product can be sold in order to increase plant profit due the widely use in industry such as food industry, pharmaceutical and personal care applications, botanical extracts, anti-freeze and chemical intermediate.

2.3 Technological option for biodiesel production

Today, most of the large scales of biodiesel plants were run base on alkali-catalyzed system due the high efficiency, low operating cost and less corrosive. But there are some disadvantages using that method which is the process is very sensitive to purity of reactant such as water and FFA content.

In addition, in order to reduce the cost of raw material, waste cooking oil used with high FFA. To ensure the good conversion acid catalyst provided as an excellent ways for feedstock with high FFA. The process gives quite high yield in esters. But, the process of reaction is slow which needed almost one day to accomplish. Despite the reaction can cause corrosion. Therefore, the method is less preferable in industry.

Other than that, there are attempts to use supercritical method (Kusdiana and Saka, 2001). By using that method, it shows that the FFA in the oils converted completely into fuel which the higher reaction rate experimentally. The method also can acceptable for wide variety feedstock. However, the process involves the high temperature and pressure will cause huge safety and expansive cost, thus is less preferable for the commercially.

Another similar approach to ultrasonic is by using hydrodynamic cavitation. An experimental works for biodiesel production with, the help of ultrasonic and hydrodynamic cavitation was done by Jianbing *et al.*, (2009). Their result shows that the equilibrium reaction time was shortened in order:

Ultrasonic, hydrodynamic cavitation, mechanical stirring.



and for energy consumption the efficiency is in order:

hydrodynamic cavitation, pulse ultrasonic, mechanical stirring.



However, scale up of hydrodynamic cavitation had better opportunities than the ultrasonic reactor because of its easier generation and less sensitivity to the geometric details.

Other than using chemical-based catalyst, it is also reported that the use of enzyme such as lipase for biodiesel production (Shimada *et al.*, 1999). Using enzyme has the advantage that it has the possibility for regeneration and reuse, longer activation of the lipase and bigger thermal stability. Other than that, it protects solvents to be used in reaction and prevent enzyme particles getting together and ease of separation of product. However, the disadvantages are loss of initial activity due to volume of the oil molecule, the number of support enzyme is not uniform, and the cost is more expensive.

2.4 Supercritical methanol

2.4.1 Introduction

An alternative, catalyst-free method for transesterification uses supercritical methanol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock, free fatty acids are converted to methyl esters instead of soap, so a wide variety of feedstocks can be used. Also the catalyst removal step is eliminated. High temperatures and pressures are required, but energy costs of production are similar or less than catalytic production routes.

During the last decade, the supercritical transesterification method for biodiesel production, a process carried out at temperatures of 280-400⁰C and pressures in the range of 100-300 bar, has been extensively studied and proposed as an alternative to conventional base and acid catalyzed biodiesel production methods. Pioneered by Japanese researchers (Saka and Kusdiana, 2001), this method takes advantage of the homogeneous phase, which forms at supercritical conditions of the alcohol and triglycerides mixture, promoting fast transesterification reactions of triglycerides and simultaneous esterification of free fatty acids (FFA) without the need of a catalyst (Pinnarat and savage, 2008). Therefore, this method can process virtually any kind of raw triglyceride material, such as animal fats and waste vegetable oil, which are difficult or unfeasible to process through conventional biodiesel production methods. However, the high methanol to triglycerides molar ratios employed in almost all of the experimental studies to date, usually 42:1, remain a mayor nuisance for the development of the supercritical transesterification method at an industrial level, due to the expectedly high methanol pumping, preheating, and recycling costs.

2.4.2 Supercritical Method

Voll *et al.* (2010) remarked on the non-catalytic reaction, using alcohol under supercritical conditions at high temperatures and pressures. Thus the features of the supercritical method allows various resources such as swill oil and frying oil to be used as the feedstocks, thus

esters yield can be more than 96% (He *et al.*, 2007). Similarly, Van Kasteren and Nisworo (2007) reported that since waste cooking oil contains FFAs, adopting supercritical transesterification could offer huge advantages by erasing pre-treatment capital and running cost. Also, the presence of FFAs in feedstocks during transesterification with various supercritical alcohols does not have a significant effect on the yield (Wang *et al.*, 2007). Supercritical methanol is a high-density chemically labile vapor that cannot be compressed into the liquid state (80 bar, 240 °C). Supercritical methanol is miscible with oils and fats or FFAs (Davies *et al.*, 2005). It has been observed that supercritical methanol process for the transesterification of fats and oils can tolerate presence of higher FFAs (Imahara *et al.*, 2008).

Saka and Kusdiana (2001) stated the yield of esters produced by supercritical methanol method (SCM) is higher than that of the common method. Thus, the conversion of FFAs to methyl esters in supercritical process led to the increase yield. In common method, FFAs, is converted to saponified products by the alkaline catalyst. The authors recently found that these same FFAs are converted to methyl esters through the dehydration reaction during the supercritical treatment of methanol (Davies *et al.*, 2005). Further, Imahara *et al.* (2008) noted that non-catalytic supercritical methanol technologies are attractive processes in biodiesel production by overcoming problems such as incomplete conversion of oils/fats because of presence of FFAs.

Banerjee and Chakraborty (2009) noted that non-catalytic supercritical transesterification of WCO has provided biodiesel of high purity (99.8%) and almost pure glycerol (96.4%). It has been also reported that, supercritical methanol with a co-solvent process is superior to the conventional supercritical methanol method, thus providing more than 98wt% yield of methyl esters (Wang *et al.*, 2007). Additionally high conversions of 80–100% were recorded when the reaction was conducted in supercritical methanol and ethanol. However, reaction catalyzed by an enzyme in supercritical carbon dioxide provided low conversions of 27–30% (Madras *et al.*, 2004).

2.4.3 Flowsheet of supercritical methanol

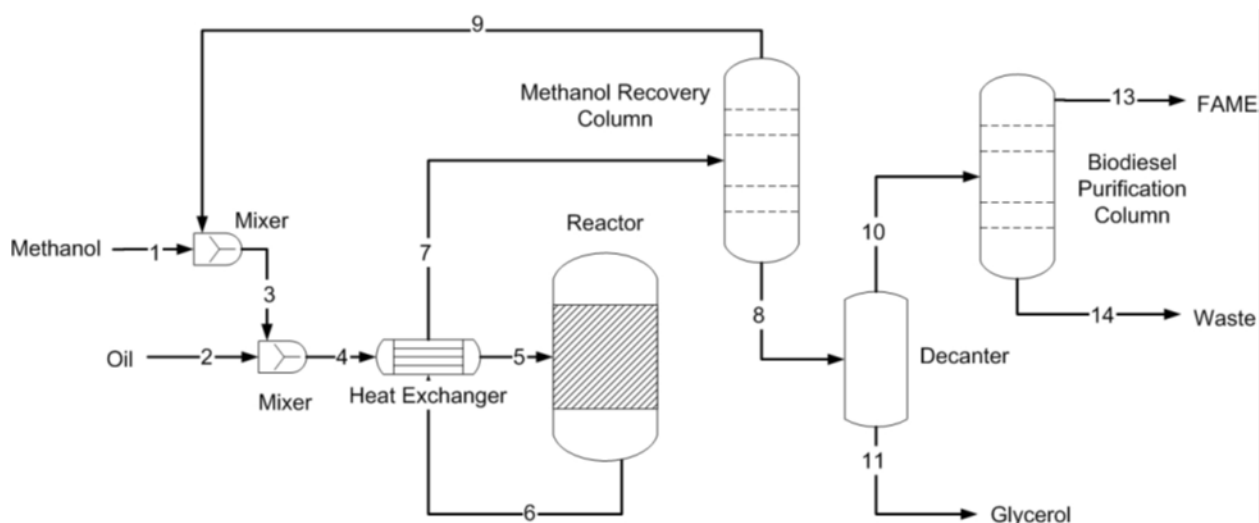


Figure 2.6: Flowsheet for supercritical methanol (Lim *et al.*, 2009)

The flowsheet of supercritical methanol configuration is shown in figure 2.6 base on the research Lim *et al.* (2009). In this work, the reaction condition with 42:1 methanol to oil molar ratio, temperature at 350°C and pressure at 430 bar are used. According to Lim *et al.* (2009), at this condition, the reaction takes only four minutes with the yield of 95%. Because of the high temperature of the reactor output stream, the heat is utilized to preheat the reactor input stream using heat exchanger while maintaining the product below 250°C. The reaction product then enters the methanol recovery distillation column with 12 theoretical stages and the reflux ratio of 0.5. Nearly 99.6% of the excess methanol can be recovered with the purity nearly 99.9%. This recycled methanol is mixed with the fresh methanol feed of 114 kg/hr before being fed again, together with oil, to the reactor.

The bottom stream of the column is then cooled down before being sent to a decanter. Based on the component density, the upper part contains 94.7% biodiesel and the rest is unreacted oil and other impurities. The bottom stream contains over 92% of glycerol and the rest is mostly methanol. As the purity of glycerol meets the commercial standard, no further purification step is needed. The biodiesel rich stream still needs to undergo further purification.

The stream is fed to a biodiesel purification column using eight theoretical stages with the reflux ratio of 0.05 and under vacuum. The biodiesel purity at the distillate stream achieves the product specifications of more than 99.6wt%.

2.5 Environmental Assessment

An environmental impact assessment is an assessment of the possible positive or negative impact that a proposed project may have on the environment, together consisting of the environmental, social and economic aspects. The purpose of the assessment is to ensure that decision makers consider the ensuing environmental impacts when deciding whether to proceed with a project. According to Young and Cabezas (1999), they have introduced a so-called waste reduction (WAR) algorithm for assessing environmental impact of a chemical process design. The concept of potential environment impact (PEI) in the WAR algorithm is based on the conventional mass and energy balance conducted at the manufacturing level. PEI is a relative measure of the potential for a chemical to have an adverse effect on human health and environment. The result of the PEI balance is an impact index that provides quantitative measure of the impact of the waste generated in the process.

Apart from that, there are some advantages to use this algorithm which is simple to use and easy to find the parameters. Furthermore, it is inherently flexible, which allows the user to emphasize or de-emphasize the individual impact categories in the calculation of the pollution indices to address their specific needs. Because of its suitability in assessing environmental performance at the design stage, the WAR algorithm has been integrated into several process simulators such as ChemCAD, Integrated Computer Aided System (ICAS) and AspenTech.

In addition, establishment of standardized and commonly accepted environmental methodology has a long way to go. There are still efforts to identify or improve ways to measure environmental performance of a system. None of the fore mentioned methodologies have become a standard or approved method to assess environmental effects of a process design. Different organizations or individuals may use different methods based on their preferences. The adoption of a particular indicator is significantly important, especially in the initial stages of process design, so that the indicator presents a direct correlation among flows and impacts and